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Influence of *f*-Electron Hopping On Valence Transition of Mixed-Valent Systems

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Abstract

The contribution of *f*-electron hopping has been studied on a four-site square cluster in an exact diagonalization method using extended Falicov-Kimball model. It appears that *f-f* hopping shifts the critical *f*-level energy (*Ec*) at which valence transition occurs. So far entropy is concerned, *f-f* hopping increases disorder in the system. Both, single and double-peak structures are obtained in specific heat curves. The peak height decreases with higher negativity of *f*-electron hopping. That indicates a reduction in the number of the density of states. Spin susceptibility (χ) characteristics show Curie-like nature as well as antiferromagnetic ordering which grows with *f-f* hopping.

Keywords: Mixed-valent systems; Falicov-Kimball model; *f*-electron hopping

INTRODUCTION

The surprising properties observed in mixed-valent (MV) compounds are highly interesting to the physicists still now [1, 2]. Phase transition in these compounds occurs due to change in temperature or pressure [3]. Mainly resonance transitions take place between states $4f^n$ and $4f^{n-1}$ with one e^- in the conduction band. As a result mean number on *f*-electrons per site (valence) becomes mixed or non-

integral. Unique electronic and thermal properties of MV states are verified from experiments of specific heat [3], the Hall coefficient [4, 5], and the optical reflectivity [6] at low temperature. All these suggest that these compounds are paramagnetic semiconductors at low temperature but poor metals at room (high) temperatures. The anomalous physical properties of MV systems have been investigated enormously within Falicov-Kimball Model (FKM) [7] and its variants [8-10]. Spinless FKM is successful to describe intermediate valence transition under external pressure, charge ordering and specific heat in rare-earth and transition metal compounds [11, 12]. The spin version of the FKM has been used [8, 13] to describe the issue of magnetic ordering and to consider the spin degrees of freedom in the MV systems.

The effect of correlated hopping interaction has been investigated within extended FKM [14] and it appeared that stronger correlated hopping interaction favors sharper discontinuous insulator to metal transition. The next-nearest-neighbor (NNN) hopping of *d*-electrons facilitates the ordered phase in the MV systems. It decreases the degeneracy of the ground state and has some signatures on the spin susceptibility [9]. The characteristics of valence transition and the ground state phase diagram are strongly changed with the addition of the nonlocal Coulomb interaction within FKM [15]. The effect of the spin dependent *f-d* interaction (Hund coupling) in MV phenomena has been investigated within FKM extended by the spin interaction [16]. It is observed that the spin interaction increases the width of valence transition and the growth of antiferromagnetic correlations.

Using dynamical mean-field theory, the FKM has been solved exactly in the limit of large spatial dimensions [17]. First-order metal-insulator transitions are observed for a certain range of Coulomb interaction between valence and conduction electrons. Also, Curie-like behavior has been exhibited by the spin susceptibility curves. Properties of a simplified FKM extended by the Ising on-site interaction has been examined [18] on the infinite square lattice. The phase diagrams show that with an increase of magnetic field, antiferromagnetic phases become less favorable and ferromagnetic phases are the most favorable.

FKM extended by *f-f* hopping has been proposed by Batista [19]. Later, the angular resolved photoemission spectrum of the FKM with electronic ferroelectricity has been studied [20] where *d*- and *f*-electrons have different hoppings. The ground-state phase diagram of the spinless FKM extended by *f-f* hopping has been studied [21] using Hartree-Fock (HF) approximation with the charge-density-wave (CDW) instability. It has been observed that the solutions perfectly reproduce the 2D intermediate-coupling phase diagram of the FKM with *f-f* hopping. The nature of excitonic (electron-hole) bound states and the development of exciton coherence have been investigated [22] using exact numerical technique in the half-filled extended FKM with *f*-electron hopping. In [1], the influence of the f-electron hopping on the stability of the excitonic phase has been studied and an increase of the excitonic $P_{df} = \langle d^{+} f \rangle$ average has been observed.

In this communication an attempt has been made to examine the effects of the *f*-electron hopping interaction on valence transition, specific heat, and entropy of MV systems in the exact diagonalization method. Exact methods are important to study the characteristics of strongly correlated systems as it can avoid the errors introduced by the different approximations. A four-site cluster can capture phase transition including superconductivity [23, 24]. Here, we have chosen a two-band, four-site and 2D square cluster and assumed the finite cluster exact diagonalization technique [16, 23]. In spite of the presence of finite size effects in this small 2x2 cluster, the exact results may give valuable indications on the effect of *f*-electron hopping in mixed-valence phenomena.

FORMULATIONS

We start with a Hamiltonian

$$H = H_o + H' \quad (1)$$

where,

$$H = E\sum_{i\sigma} f_{i\sigma}^{\dagger} f_{i\sigma} + U\sum_{i} f_{i\uparrow}^{\dagger} f_{i\uparrow} f_{i\downarrow}^{\dagger} f_{i\downarrow} + G\sum_{i\sigma\sigma'} d_{i\sigma}^{\dagger} d_{i\sigma} f_{i\sigma'}^{\dagger} f_{i\sigma'} + V\sum_{<i,j>\sigma} (f_{i\sigma}^{\dagger} d_{j\sigma} + d_{j\sigma}^{\dagger} f_{i\sigma}) + t\sum_{<i,j>\sigma} d_{i\sigma}^{\dagger} d_{j\sigma} \quad (2)$$

This is the extended Falicov-Kimball model Hamiltonian. Here the first term *E* is the *f*-level energy, *G* denotes the strength of *f-d* Coulomb interaction, *U* represents the Coulomb interaction between *f*-electrons with opposite spins at the same site, and *V* is the *f-d* hybridization interaction. The last term *t* is the quantum mechanical hopping of the itinerant *d*-electrons between *NN* sites.

The summations are taken over all pairs of nearest neighbor (*NN*) sites on the 2D square lattice.$f_{i\sigma}$and $d_{i\sigma}$ are the usual fermion operators for *f* and *d* electrons respectively (σ, σ' = spin).
And

$$H' = t_f \sum_{<i,j>\sigma} f_{i\sigma}^{\dagger} f_{j\sigma} \quad (3)$$

Where*H'* is the electron hopping term with interaction strength t_f. The representative four-site spin is given by [16]

In our calculations the *f*-electron density$< n_i^f > = 1/N_S(\sum_{i\sigma} f_{i\sigma}^{\dagger} f_{i\sigma})$

and*f-d*intersite correlation function is$C_{fd} = < f_{i\sigma}^{\dagger} d_{j\sigma} >$

N_S= the number of lattice sites. The low temperature specific heat *C* is calculated using

$$C = k_B\beta^2 \frac{\partial^2}{\partial\beta^2} lnZ \quad (4)$$

and the entropy per lattice site is defined as

$$S = \frac{1}{N_S}\left(k_B lnZ + \frac{<H>}{T}\right) \quad (5)$$

Here$Z = \sum_{\alpha} e^{-\beta E_{\alpha}}$being the partition function of the system
and $= \frac{1}{k_B T}$, $k_B$represents the Boltzmann constant which is taken unity for simplification.

Spin susceptibility for *f*-electrons is defined by

$$\chi = \beta < (n_{i\uparrow}^f - n_{i\downarrow}^f)^2 > \quad (6)$$

RESULTS AND DISCUSSIONS

The parameters used in this work are the results obtained in different experimental observations.

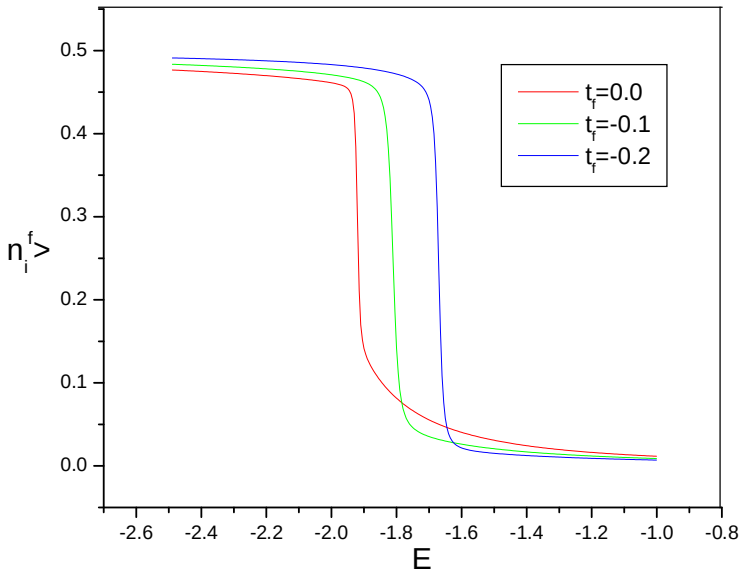

Figure 1: *f*-electron density $<n_i^f>$ vs. E for different values of t_f.
Here U=5.0, V=0.1, G=2.0, t = -1.0

For different values of *f*-electrons hopping interactions t_f, the change of *f*-electron density $<n_i^f>$ with *f*-level energy E is presented in Fig.1. In all cases a first order insulator to metal valence transition is observed with the increase of *f*-level energy. Similar valence transitions have been observed in Ref. [25, 26]. This *f*-level energy E parameterizes the external pressure. It is clear from the figure that higher negative value of *f*-electron hopping $t_f$shifts the critical *f*-level energy E_{cn}at valence transition toward higher values. So, the *f*-electron hopping t_f alters both the reference *d*-level energy and the critical value of *f*-level energy E=E_c.

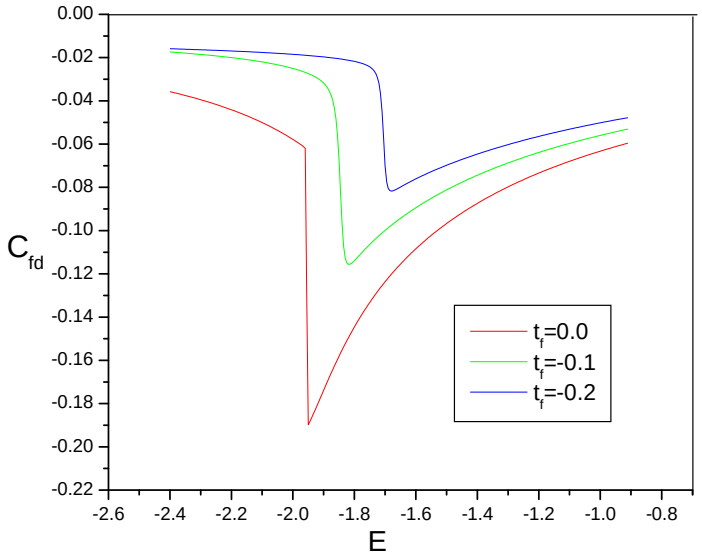

Figure 2: *f-d* correlation function C_{fd} vs. E for different values of t_f.
Here U=5.0, V=0.1, G=2.0, t = -1.0

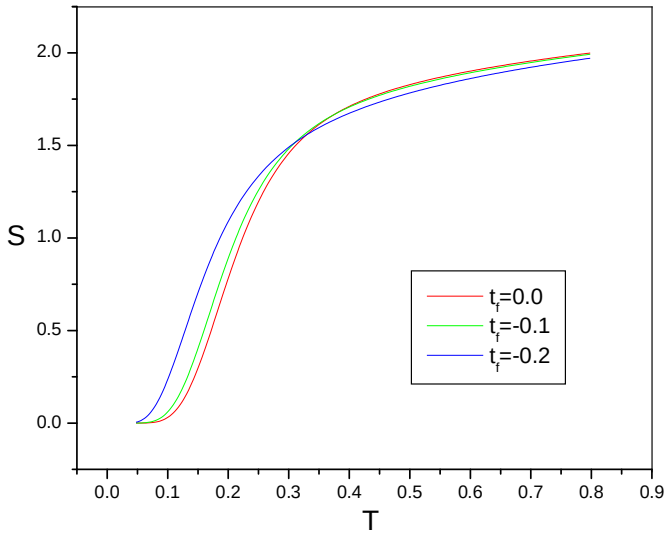

Figure 3: Temperature dependence of entropy *S* for different values of t_f.
Here *E*= -1.5, *U*=5.0, *V*=0.1, *G*=2.0, *t* = -1.0

Fig.2 shows the variation of *f-d*excitonic correlation function with*E* for various values *f*-electrons hopping t_f. It is established that this correlation C_{fd} has a very small negative value close to zero in the insulating and metallic phases [27], changes when intermediate valence transition occurs at a certain *E* value (E_c). Our observations also support these arguments. It is also found that increased negative values of *f*-electron hopping t_f keeps C_{fd} closer to zero value and shifts the lowest C_{fd} point towards higher *E* values. This confirms the previous observation of shifting the value of E_c with *f*-electron hopping interaction t_f.

Variation in entropy S with temperature *T* is shown in Fig.3. The nature of the curves is same for all three different values of t_f. With the increase of temperature; entropy increases and gradually becomes almost constant at higher temperatures. At the lower temperature region ($0.05 < T < 0.3$), the differences between different values of *f*-electron hopping curves are clearly noticeable, as it is maximum in this region. At *T*=0.35, all curves converge, and above this temperature system approaches to complete disorder when entropy increases slowly being nearly independent of t_f.

Figures 4 and 5 represent the variation of low temperature specific heat *C* with temperature. We take $E > E_c$ in Fig.4 for different values of *f*-electron hopping t_f. Specific heat curves show a broad single peak structure when $E > E_c$. The ground state degeneracy is small and many body state distributions are binomial in this energy region. The highest value of specific heat decreases and the peak shifts to lower region of temperature when negativity of t_f is increased.

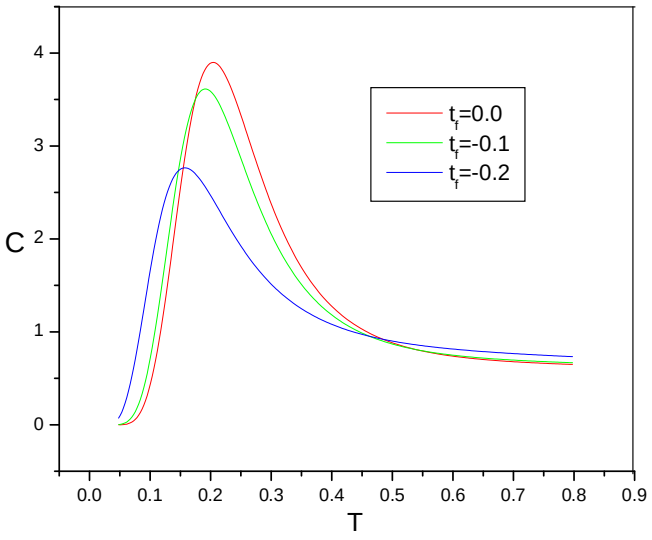

Figure 4: Temperature dependence of specific heat *C* for different values of t_f.
Here *E*= -1.5, *U*=5.0, *V*=0.1, *G*=2.0, *t*= -1.0

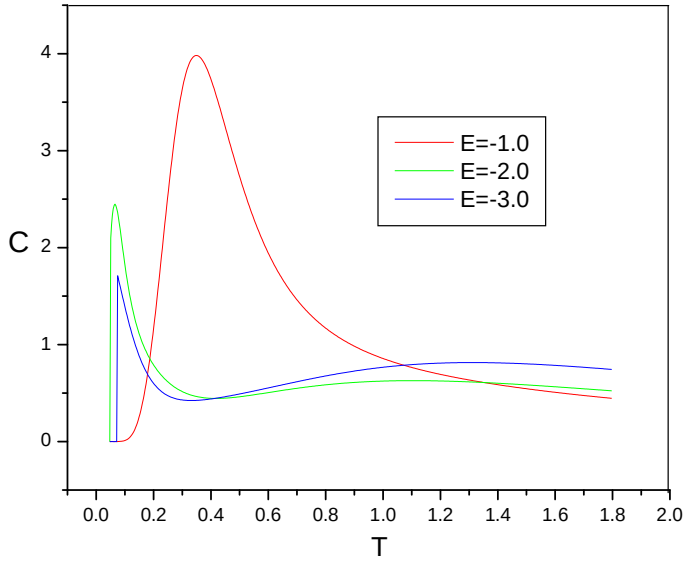

Figure 5: Temperature dependence of specific heat *C* for different values of *E*.
Here t_f= -0.1, *U*=5.0, *V*=0.1, *G*=2.0, *t* = -1.0

Figure 5 shows variation of specific heat when *f*-electron hopping t_f= -0.1 with different values of *f*-level energy *E*. A two peak structure[1] is obtained for $E < E_c$(e.g. when *E* = -2, -3). A large number of many-body states with degeneracy of ground state are responsible for the occurrence of first sharp peak. The very flat second Schottky type peak appears in a broad region of temperature. Here also the distribution of many-body states is binomial in nature. Experiments with mixed-valence *SmS* confirm this double peak structure of specific heat *C*. At very low temperatures, the curves follow $C \sim T^2$(approximately) contrary to Fermi-liquids ($C \sim T$) [28]. This is in good agreement with Ref. [29].

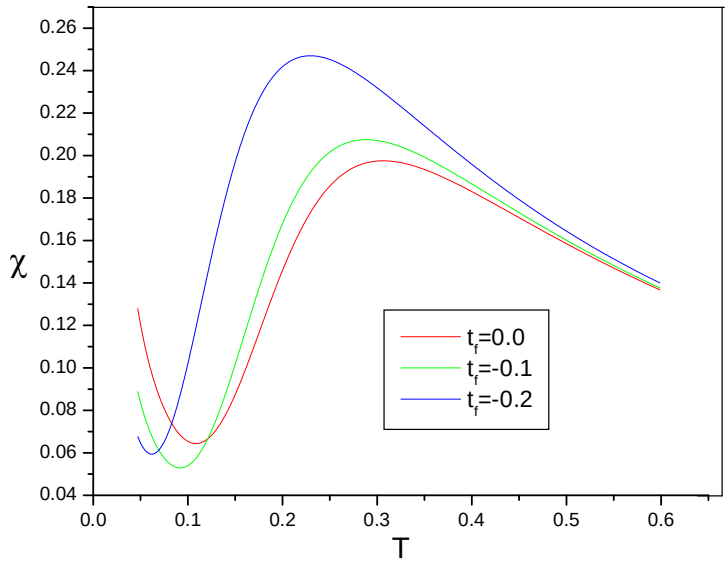

Figure 6: Temperature dependence of spin susceptibility χ for different values of t_f. Here E= -1.5, U=5.0, V=0.1, G=2.0, t = -1.0

The spin susceptibility χ against temperature T is plotted in Fig.6. The susceptibility curves are peaked at the lower temperature region. This is due to magnetic ordering and Curie-like behavior of χ. The peak value of χ gradually increases and shifts to lower temperature region with the increase of negative values of *f*-electron hopping t_f, thus raises the growth of antiferromagnetic correlations. This characteristic of susceptibility variation with temperature is experimentally found in mixed-valent*TmSe* [30] which is antiferromagnetically ordered at very low temperatures. Unlike Fermi-liquids, the susceptibility is temperature dependent. The maxima in specific heat (Fig. 4) and spin susceptibility χ (Fig. 6) occur at the same temperature approximately, confirming previous results [16, 31].

CONCLUSIONS

Like *d*-electron hopping, it has been identified that f-electron hopping also has certain important roles on mixed valence phenomena. It shifts the value of critical *f*-level energyE_c towards higher values. *f-d*excitonic correlationC_{fd}also confirms this shifting of E_c. Entropy (a measure of disorder) increases with *f-f* hopping. Specific heat curves show single peak for *E>Ec* and double peak when $E \leq Ec$. The first one is a sharp peak at lower temperature and the second broad peak at higher temperature is Schottky type. Variation of spin susceptibility χ with temperature shows antiferromagnetic type of ordering at low temperatures. A peak at small temperature indicates Curie contribution to susceptibility. Non-Fermi liquid nature of the system has been identified from the finite temperature properties.

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